The Other Side of the Coin: Geochemistry of Alkaline Lakes in Volcanic Areas

Giovannella Pecoraino, Walter D'Alessandro, and Salvatore Inguaggiato

Abstract

Among surface waters, lakes in volcanic areas display the greatest range in pH values: from negative values up to about 12. The present chapter is a short review of the main features of alkaline lakes, which belong to the high-pH part of this range. They are characterised by saline or hypersaline waters, pH values higher than 9 and high Na^+, HCO_3^- and CO_3^{2-} and low Ca^{2+} concentrations. Alkaline lakes are found in quiescent or recently extinct volcanic areas where neither water vapour nor acidic magmatic gases can reach surface waters. Their occurrence depends on peculiar climatic and geological conditions that allow evaporative concentration of the water (potentially evaporation much higher than water inputs and in endorheic basins) and on geochemical factors that favour a chemical evolution towards an alkaline environment (composition of the dilute input waters characterised by a ratio between total dissolved inorganic carbon and earth-alkaline elements much higher than 1). Such initial composition, due to evaporative concentration, after the deposition of earth-alkaline carbonate minerals, will lead to the above-mentioned typical composition. Alkaline lakes also host microbial communities sometimes characterised by extremely high productivity. These microbial communities are scientifically remarkable because they comprise some interesting extremophiles, which can grow not only at very high pH and salinity conditions but also in the presence of elevated concentrations of toxic elements (e.g. As, Se, Te).

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1 Introduction

The word "volcanic lake" is instinctively linked to a hot and acidic water body (Christenson et al., this issue). Indeed this is true in active volcanic systems where water vapour and acidic magmatic gases (mainly SO_2 and HCl) have the possibility to directly reach a lake and the dissolution of the gases will necessarily lead to high temperatures and very low pH (<0) values of the lake water (Christenson and Tassi, this issue). As widely shown in the previous chapters, such extreme conditions will consequently lead to very high salinities and unusual chemical compositions do to intense water-rock interaction processes (Varekamp, this issue).

But, if we look at the compilation of pH values in volcanic lakes made by Varekamp et al. (2000) and Marini et al. (2003) we can observe that, although clustering around a few acidic values, they span over a wide range with alkaline values being not too rare. Furthermore, it should be considered that the compilation is probably biased towards acidic values because acidic lakes are both more attractive to study and their regular survey is important for estimating the activity of the related volcanic system (Giggenbach 1990; Rowe et al. 1992; Aguilera et al. 2000; Varekamp et al. 2000; Marini et al. 2003; Taran et al. 2008).

In some active volcanic areas acidic magmatic gases do not have the possibility to reach surface water bodies. This is generally due to the presence of hydrothermal systems at depth. The most soluble of the magmatic gases (like SO_2, HCl and HF) interacting with the hydrothermal system dissolve in the liquid phase forming mainly anionic species (SO_4^{2-}, Cl^- and F^-). This process leaves the residual gas phase enriched in CO_2. The latter is also the main component of the gases released in quiescent or recently extinct volcanic areas.

The fate of the abundant upflow of CO_2 upon interaction with surface water bodies depends on their chemical and hydrological characteristics. Carbon dioxide can passively accumulate as dissolved gas in the deepest layers of the lakes leading to dangerous pressure build up that eventually could evolve in deadly massive gas releases (Kusakabe, this issue; Vaselli et al., this issue). The most known examples are the fatal episodes happened at the Cameroonian lakes Monoun and Nyos in the 1980s, which led to 37 and more than 1,700 casualties, respectively (Witham 2005; Kusakabe, this issue and references therein). The abundant geogenic CO_2 also contributes to weathering reactions within cold or thermal aquifers that release alkalis and bicarbonate to the groundwater. Such waters emerging at the surface, together with the right climatic and hydrological conditions, can possibly lead to the formation of alkaline lakes.

Alkaline or soda lakes are a peculiar type of saline lakes whose waters display pH values above 9 and whose chemical composition is characterised by Na^+ as the main cation and by the presence of high HCO_3^- and CO_3^{2-} contents. Nevertheless, sometimes the main anionic species are Cl^-, or rarely SO_4^{2-}. In the most extreme cases of evaporation (e.g., Magadi Lake, Kenya) the salinity may reach values at or near halite saturation, and the concentrations of carbonate may be very high (up to thousands of meq/l). The pH of such brines may reach 10–11 or even higher (Grant and Tindall 1986). Trona ($NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$) and Natron ($Na_2CO_3 \cdot 10H_2O$) often precipitate in such environments. Examples of the chemical composition of alkaline lakes in volcanic areas are displayed in Table 1.

One of the most striking features of many soda lakes is their colour. Depending on the water chemistry of the individual lakes, they are likely to be green, pink, red or orange, due to massive permanent or seasonal blooms of microorganisms (Grant et al. 1990; Christenson et al., this issue). This is reflected in the extremely high primary productivity and wide variety of microbial life associated with some of these lakes.

Table 1 Location and chemical composition of some alkaline lakes

Name	Northing	Easting	Altitude (m)	pH	Na (meq/l)	K (meq/l)	Mg (meq/l)	Ca (meq/l)	F (meq/l)	Cl (meq/l)	SO_4 (meq/l)	Alk (meq/l)	SiO_2 (meq/l)	Ref.
Van lake (Turkey)	38° 39.926′	42° 54.190′	1,647	9.88	347	11.1	9.06	0.17		166	50.8	156	7	Reimer et al. (2009)
Mono lake (USA)	38° 00.422′	−119° 00.379′	2,031	10.00	1,331	45.6	2.72	0.20		518	208	593	14	Johannesson et al. (1994)
Albert lake (USA)	42° 37.727′	−120° 14.139′	1,357	9.71	1,975	33.2	0.04	0.10		1,175	37.4	699	96	Johannesson et al. (1994)
Abiyata (Ethiopia)	7° 36.300′	38° 35.976′	1,581	10.08	430	9.57	0.02	0.03	16	119	10.0	316		Gizaw (1996)
Langano (Ethiopia)	7° 35.607′	38° 45.484′	1,587	9.05	19	0.59	0.23	0.39	1	5.08	0.35	15.5		Gizaw (1996)
Magadi lake (Kenia)	−1° 55.243′	36° 16.039′	606	10.77	4,826	53.5			104	2,474	45.0	1,218	1,100	Jones et al. (1977)
Bogoria lake (Kenia)	0° 15.401′	36° 05.788′	991	9.20	1,778	16.5	0.16	1.70		255	11.4	1,550		Renaut et al. (1986)
Nau Co (China)	32° 49.305′	82° 12.224′	4,381	9.50	3,087	128	21.4	0.20		1,374	1,496	50.8		Zheng et al. (1993)
Atlacoya (Mexico)	19° 07.637′	−97° 32.486′	2,381	10.70	233	7.70	0.09	0.21		31.9	1.03	121	34	Vilaclara et al. (1993)
Cachi laguna (Bolivia)	−21° 44.054′	−67° 56.729′	4,499	10.05	4,000	910	0.24	0.30		1,610	746	2,500	432	Risacher and Fritz (1991)
Specchio di venere (Italy)	36° 48.668′	11° 59.089′	2	9.20	313	13.7	0.50	12.10		260	22.9	59		Aiuppa et al. (2007)

This review chapter highlights the geological, hydrological and climatic conditions occurring in the formation of alkaline lakes and the geochemical processes leading to high salinity and high pH waters. Some case studies in volcanic areas are discussed and finally, an overview of the rich and peculiar microbial life in alkaline lakes is given.

2 Hydrological and Geochemical Processes in Alkaline Lakes

2.1 Occurrence of Alkaline Lakes

Alkaline lakes are mostly found within closed (endorheic) basins and their occurrence depends on the combination of climatic (amount of rain waters, evaporative processes), geological/topographic and geochemical (gas-water-rock interactions) factors.

The climate provides an important function in the water balance of endorheic lakes, because it regulates the water supply coming into the basin as rain and runoff, and it determines the evaporation rate. The inflow, generally limited, must be sufficient to sustain a permanent lake. Arid and semi arid climates, where potential evaporation is always higher than the meteoric recharge, are the ideal location to form saline lakes and consequently alkaline lakes.

Geological/topographic conditions allow, or do not, the development of a closed basin (morphology of the site = closed basin, presence of springs, impermeability of shallow strata, absent or near absent outflow, etc.). Many soda lakes were formed within volcanic craters or calderas (e.g., Mono Lake, USA, and Specchio di Venere, Pantelleria Island, Italy), within a graben in areas characterised by extensional tectonics (like the lakes of African Rift Valley, e.g., Natron Lake, Kenya) or upon abrupt interruption of a riverbed by lava flows or lahars (e.g., Lake Van, Turkey Pátzcuaro Lake, Mexico). Furthermore, the presence of regional tectonic or volcano-tectonic structures favours the input to the lake of thermal waters charged with endogenous carbon dioxide, important in the evolution of alkaline lakes. The topography can also strongly influence the climate of the area creating arid conditions due to a rain shadow. A particular morphology is represented by the Lonar Lake, in India, that was formed by a high velocity meteorite impact on basaltic rocks of the Deccan traps about 50 ka ago (Wani et al. 2006; Deshmukh et al. 2011).

The chemical composition of rocks (through weathering), of groundwater, spring or surface water flowing into the lake, the presence of dissolved CO_2, and mineral precipitation-dissolution all control the final chemical composition of the lake water. According to Spencer et al. (1990), in the case of evaporative processes, water assumes a composition that is a function of the original, initial dilute composition. The evaporation induces oversaturation and the first solid phases that are precipitated are alkaline-earth carbonates. At this stage the ratio between total dissolved inorganic carbon (TDIC) and the main alkaline–earth species (Ca^{2+} and Mg^{2+}) will be the main parameters that will drive the evolution of the evaporating lake towards an alkaline composition or not (Hardie and Eugster 1970).

2.2 Water and Solute In- and Outputs

Four main types of input can generally be recognised (Volkova 1998; Jones and Deocampo 2003; Aiuppa et al. 2007; Jones et al. 2009):

1. Meteoric recharge occurs either directly to the lake surface or through the runoff along the hydrologic basin. Depending on climate, it could be a more or less important part of the water input. The solute input is generally limited for the part attaining to the direct recharge while runoff could play a significant role in dissolving previously precipitated salts along its shores.
2. Focused discharge occurs through springs from the drainage area or diffuse seeps percolating slowly through the shores. They can represent an important part of both water and solute recharge to the lake. A slow flow rate may

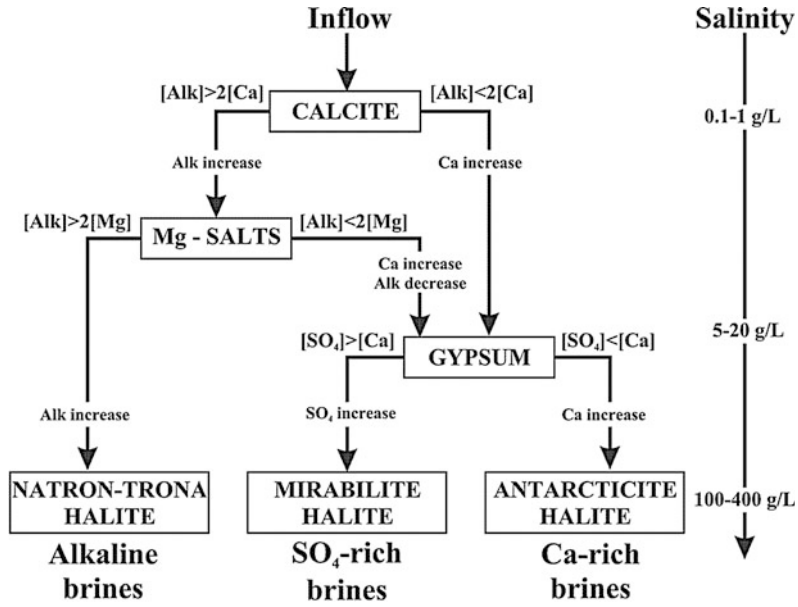

Fig. 1 Flow diagram showing both the geochemical brine evolution and mineral precipitation sequence during evaporative phenomena of lake waters. Solute constituents are indicated by *square brackets*, mineral precipitates are indicated by *boxes* (modified after Hardie and Eugster 1970; Eugster and Jones 1979)

induce an incipient evaporation of the waters before they reach the main body. In volcanic environments such input sometimes derives from geothermal systems and the water chemistry can be modified by precipitation of solid phases at the spring mouth induced by rapid changes in physico-chemical conditions (temperature drop, loss of CO_2, shifting of redox equilibria towards more oxidising conditions).

3. Rivers, generally of short length and low discharge due to the usually small area of their drainage basin can feed the lake.
4. Underground waters fill aquifers in the drainage basins. They discharge into the lake underwater through springs and seeps. Their contribution in terms of water and solute input can be variable and is often difficult to quantify depending on many geological and hydrological conditions.

As alkaline lakes are found almost always within closed basins, only three outputs can be recognized (Jones and Deocampo 2003 and references therein, Stumm 2004):

1. Evaporation accounts for the main output of the lake water, although generally without losing solutes;
2. Infiltration to the groundwater is generally limited in terms of water loss and can also be a significant solute output;
3. Precipitation of solid phases due to oversaturation of the lake waters accounts for the main loss in solutes (Fig. 1).

2.3 Geochemical Evolution

Waters undergoing evaporative concentration precipitate a sequence of minerals in order of increasing solubility. Hardie and Eugster (1970) and Eugster and Hardie (1978) introduced the basic concept of "chemical divide" to account for the evolution of solute concentration during evaporation.

The whole process is graphically shown in Fig. 1 which accounts for most natural waters. The reaching of oversaturation for a few minerals plays an important role in the water evolution. The least soluble minerals (i.e. the first to precipitate) are carbonates ($CaCO_3$ and $MgCO_3$), followed by gypsum ($CaSO_4 \cdot 2H_2O$). The mineral forming ions (both cations and anions) are removed from the water solution as they contribute to the solid phases. When the mineral precipitates, the solubility product ($K_s = [X^-]\cdot[Y^+]$) must remain constant and the more abundant constituent in solution becomes dominant with respect to the others (i.e. during

$CaCO_3$ precipitation, if Ca increases the C species decrease or vice versa). The outcome of this process is the generation of three main groups of brines: alkaline (Na^+/HCO_3^-–CO_3^{2-}–Cl^-), sulfate-rich (Na^+/SO_4^{2-}–Cl^-) and calcium-rich (Na^+–Ca^{2+}/Cl^-) brines.

As such, the final composition of the brines strongly depends on the initial composition of the dilute water. A small variation of the initial ratio of the critical components in the dilute water TDIC/Ca^{2+} and TDIC/(Ca^{2+} + Mg^{2+}) may cause drastic changes in the final brine composition. In turn, the composition of dilute inflow waters is mainly inherited from rock alteration. Therefore, there is an overall relationship between lithology and the final lake water composition. Each broad type of lithology is reflected in the composition of the dilute water which is further amplified by evaporative concentration. In a pioneering study, Garrels and Mackenzie (1967) first evidenced the strict relationship between igneous rocks and alkaline brines. High-purity igneous rocks are composed of silicate minerals being almost devoid of anionic components (Cl^-, SO_4^{2-}). The only available anion that can balance the cations derived from the weathering of pure igneous rocks is HCO_3^-, which is, in active and recently extinct volcanic areas, mainly derived from CO_2 of endogenous origin. Weathering of silicate minerals produces HCO_3^- and cations through silicate hydrolysis (Eqs. 1 and 2). The cations produced in a silicate hydrolysis reaction reflect the cations in the mineral being weathered. For instance, minerals with high Na content would tend to yield Na^+ when subjected to hydrolysis. Weathering of granitic and rhyolitic rocks (or sediments derived from them) is a common means of producing alkaline waters, as these rocks are composed primarily of K-feldspar, quartz, and Na-plagioclase, with generally little Ca (Eq. 1). Therefore, hydrolysis of granitic and rhyolitic rocks will yield HCO_3^-, Na^+, and K^+, but minor Ca^{2+} contents:

$$\mathrm{CO_2 + H_2O + \text{rhyolite (Na-plagioclase; K-feldspar; quartz)} \Rightarrow \text{clay minerals} + K^+ + Na^+ + HCO_3^-} \quad (1)$$

As a result, waters whose chemistry is controlled by silicate hydrolysis of granitic/rhyolitic rocks will have $HCO_3^- \gg Ca^{2+}$. This explains the presence of alkaline waters in granitic/rhyolitic terrains, but such waters are found also in areas dominated by andesitic/basaltic lithologies whose weathering reactions can be summarised as follows:

$$\mathrm{CO_2 + H_2O + \text{basalt (plagioclase; olivine; pyroxene)} \Rightarrow \text{clay minerals} + Ca^{2+} + Mg^{2+} + Na^+ + HCO_3^-} \quad (2)$$

In these cases, the silicates are more reactive due to their smaller grain sizes and to the presence of mafic minerals and/or volcanic glass (Jones 1966); the fast silicate weathering rates lead to a hydroxyl-neutralizing reaction

$$Ca^{2+} + HCO_3^- + OH^- \Rightarrow CaCO_3 \downarrow + H_2O \quad (3)$$

that effectively removes alkaline earths from solution, and produces alkaline waters (OH^- consumption) (Jones 1966).

Although examples of pH as high as 11–12 in soda lakes can be found in literature (Grant et al. 1990; Jones et al. 1998) these cases are rare. Pure sodium carbonate solutions have pH values of 11.3–11.5. The contact with atmospheric CO_2 and the presence of other salts, which is the real situation in the soda lakes, result in lower pH values. The sodium carbonate/bicarbonate system has its maximum buffering capacity in the pH range 9.5–10.2. Therefore, the most common pH values for soda lake waters can be expected to be found within this range, unless other buffering systems are dominating.

A useful tool to represent the compositional trend of water during evaporation is the Spencer diagram (Fig. 2): it is a Ca^{2+}, SO_4^{2-}, HCO_3^- + CO_3^{2-} (expressed in equivalent/l) ternary phase diagram in which three compositional fields, divided by compositional lines (the "chemical divides"), are indicated. The diagram shows how inflow waters evolve in composition due to evaporation and mineral precipitation. Arrows starting from the composition of the forming solid phase evidence precipitation processes. If calcite is the first mineral to precipitate (inflow water in the lower right compositional field), the water evolution always follows a trend that diverges from the calcite compositional point

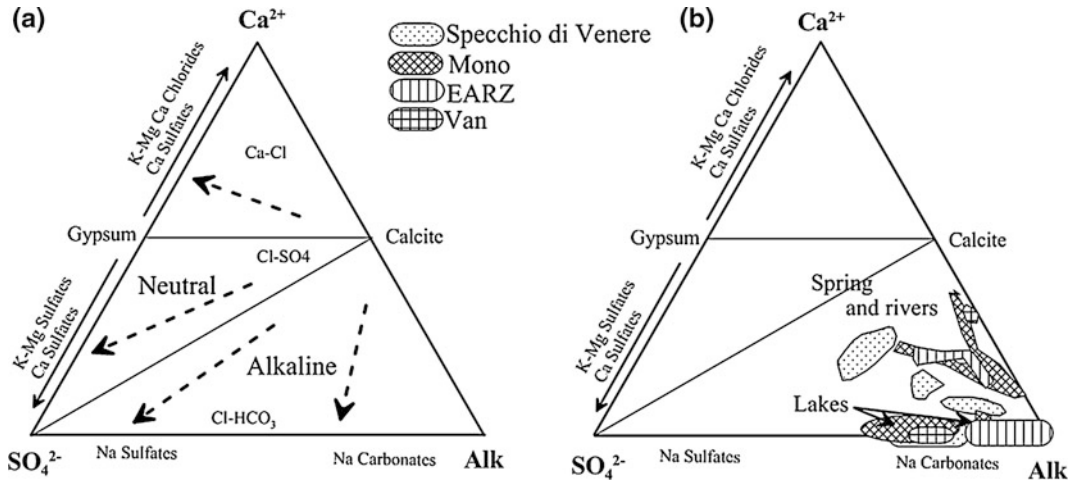

Fig. 2 **a** The spencer ternary phase diagram with compositional trends (*arrows*) of different composition evaporating waters indicated (see text for explanations); **b** some example of inflow waters (initial original composition) and lake waters (final composition) based on literature data

(Fig. 2a) becoming Ca-poor and Na, Cl, SO_4-enriched depending on the initial water composition. Waters in the Ca–Cl field evolve towards the Ca vertex as a consequence of SO_4 and HCO_3 depletion due to precipitation of calcite and gypsum. Some examples based on literature data are shown in Fig. 2b.

Due to evaporative concentration and high solubility in alkaline environments many trace elements can reach very high contents in alkaline hypersaline lakes. This could be of concern for their often high toxicity (Ochieng et al. 2007). But sometimes this could lead to elevated concentrations of elements of high economic value. For example Li and REE elements are sometimes extracted from highly concentrated brines obtained from the evaporation of the waters of alkaline lakes.

3 Geographical Distribution

Figure 3 shows the position of the alkaline lakes that were considered for the present review. As seen before among the conditions that favour the formation of an alkaline lake there is the presence of an arid or semi-arid climate, consequently there is no surprise to find them prevailingly in sub-tropical regions. These areas are the site of high atmospheric pressure feeding divergent atmospheric circulation cells. The greatest deserts are all found along this belt (Sahara, Arabian desert, central Asia deserts, Mexican and western USA deserts, Namibia, Australian desert).

The probability for a certain area to host one or more of these lakes greatly increases if the area is also endorheic and is, or was in the recent geological past affected by volcanic activity. Most of the alkaline lakes considered in this review are concentrated along the East African Rift Zone (EARZ hereafter, Lake Magadi and Lake Bogoria) (Talling et al. 1973; Melack and Kilham 1974; Jones et al. 1977; Melack 1979; Macintyre and Melack 1982; Yuretich and Cerling 1983; Renaut et al. 1986; Cerling 1996; Gizaw 1996; Grant et al. 1999; Deocampo 2005; Ochieng et al. 2007; Oduor and Schagerl 2007; Ayenew 2008; Dawson 2008; Ma et al. 2011).

The EARZ is an area of recent intense volcanic activity and also represents an endorheic area stretching about 4,000 km along the eastern part of Africa. The entire area is filled by thousands of lakes of different sizes. Despite its position close to the equator, precipitations are often rare due to a rain-shadow effect. Such

climatic and hydrologic conditions led to the formation of many saline lakes, most of which are also alkaline.

Two other areas in which many alkaline lakes are present are the south-western part of North America, e.g. Western USA (Mono Lake and Albert Lake) and Mexico (Lake Atlacoya) (Anderson 1958; Castenholz 1960; Jones 1966; Bischoff et al. 1993; Vilaclara et al. 1993; Johannesson et al. 1994; Connell and Dreiss 1995; Neumann and Dreiss 1995; Bischoff et al. 2004; Oremland et al. 2004; Baesman et al. 2009; Sahajpal et al. 2011) and the central-southern part of the Andean chain in South America (Laguna Cachi, Bolivia; Fig. 3). Both areas are within the volcanically active Ring of Fire around the Pacific Ocean. In the latter area, which comprises the territories of Bolivia, Chile and Argentina (Risacher and Fritz 1991; Risacher et al. 2003), notwithstanding the necessary hydrologic and climatic conditions, alkaline lakes are not as widespread as expected. For example, in their review on saline lakes of northern Chile, Risacher et al. (2003) state that only one of the considered 226 lakes and ponds could be classified as alkaline. The authors ascribe this to the abundance of both reduced and oxidised volcanic sulfur species. The alkalinity/calcium ratio of inflow waters is consequently lowered by the oxidation of native sulfur (reducing alkalinity) and the deposition of anhydrite or gypsum transported by strong winds (increasing Ca concentration).

Another area where climatic and hydrologic conditions favour the formation of alkaline lakes is the central part of Asia (Fig. 3) stretching from the Caspian Sea in the west to China (Tibet and Qinghai) in the east (Zheng et al. 1993; Volkova 1998; Zhang et al. 2008; Zheng and Liu 2009). Unfortunately, the literature on alkaline lakes in this area focuses on microbiology (Kompantseva et al. 2007, 2009). Despite the few notices about these lakes, the connection between the presence of alkaline lakes and recent volcanic activity of the area was highlighted by Zheng et al. (1993), at least for China.

Australia, being for its greatest part arid and composed of endorheic basins, is the host of numerous saline lakes, but the geology of the area does not create the necessary conditions for the evolution of these lakes towards alkaline conditions. On the contrary, the waters of these lakes display pH values from strongly acidic to moderately alkaline (1.7–8.6, Bowen and Benison

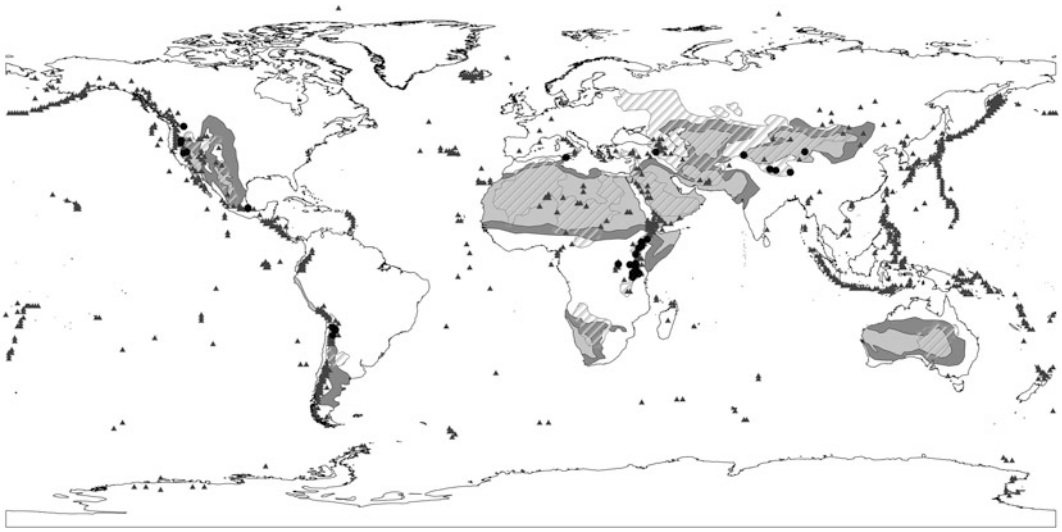

Fig. 3 Global distribution of soda lakes. Volcanoes of the ring of fire (*triangles*), soda lakes (*circles*), arid and semi-arid zones (*light gray* and *dark gray areas* respectively) and endorheic zones (*light gray shaded areas*) are indicated

2009). Most of Australia is formed by a tectonically stable Archean shield which remained above sea level exposed to weathering since the Mesozoic. As a result, the basement rocks are covered with thick zones of highly-weathered and chemically-altered regolith. In such geological framework, sulfide and Fe oxidation strongly contribute to acid formation following processes geochemically similar to those active in acid mine drainage systems (Long et al. 1992; Bowen and Benison 2009).

Even Antarctica, despite being covered for more than 99 % of its surface by a permanent ice cap, hosts some saline lakes (Green and Lyons 2009). Although some of them display pH values up to 10, no significant relation to volcanic activity or magmatic rocks has been ascertained.

4 Some Case Studies

4.1 Lake Van (Turkey)

Lake Van (Fig. 4a) is a terminal lake located on the high plateau of Eastern Anatolia (Turkey) at 1,648 m asl. This area is tectonically highly active, and earthquakes within the basin and the surrounding area of Lake Van are very frequent (Degens et al. 1984). The lake with a surface area of ca 3,600 km^2, a maximum depth of 451 m and a volume of about 600 km^3 is the largest alkaline lake and, after the drying up of Lake Aral, the third largest closed basin in the world (Landmann et al. 2011). The origin of Lake Van was ascribed to a remnant of a palaeovalley of the river Euphrates dammed about 60 ka ago by an

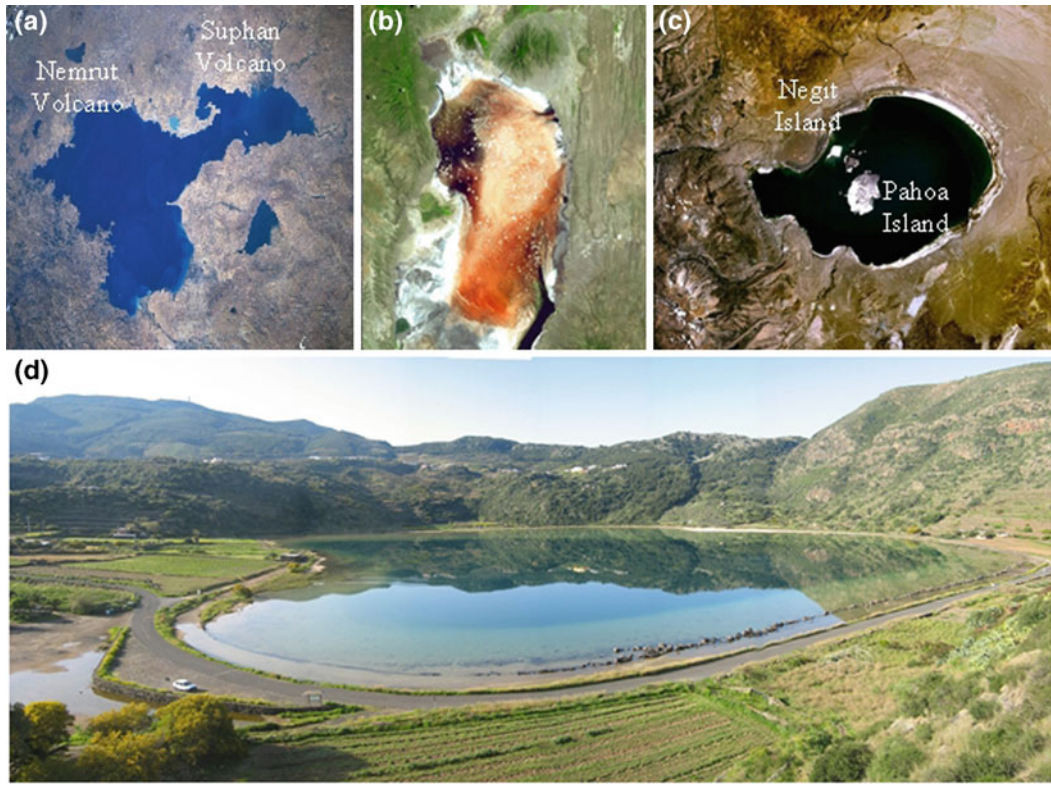

Fig. 4 Photos of selected lakes. **a** Van, Turkey. **b** Natron, Tanzania. **c** Mono, California. **d** Specchio di Venere (in Italian Mirror of Venus), Italy. *Photos* **a**, **b**, **c** from http://landsat.gsfc.nasa.gov and **d** by Walter D'Alessandro

eruption of Nemrut volcano located about 15 km west of the Lake Van (Degens and Kurtman 1978; Wong and Degens 1978; Yilmaz et al. 1998 and references there in; Utkutu 2006). Four composite volcanoes are aligned north of the lake, from WSW to ENE (Fig. 4a): Nemrut volcano (2,948 m), considered still active; Süphan volcano (4,158 m), inactive for several millennia; the older Meydan volcano (3,290 m); and Tendurek shield volcano (3,584 m) at the NE limit of the drainage area, recently active (Aydar et al. 2003). All tephra layers observed in lake cores are attributed to Nemrut volcano (Landmann et al. 1996) which erupted alkaline trachyte and basalt lavas, rhyolites and phonolites.

On the other hand, most of the drainage basin is constituted by volcanic rocks of Süphan volcano while the southern area comprises intrusive and metamorphic rocks of the Bitlis massif (Tomonaga et al. 2011). The lake has many tributaries but more than half of the runoff (highest discharge in April–May) can be attributed to Zilan, Bendimahi and Engil rivers (Reimer et al. 2009).

Christol et al. (2008) estimated a loss of 3.6 km^3 of water by evaporation and a recharge of 2.2 km^3 by rivers and 1.4 km^3 by precipitation. The lake is stratified in summer while in winter, cooling of the surface water and impact of winds induces homogeneity of water from 0 to 70 m.

Lake Van is characterised by strong seasonal oscillations in temperature, precipitation, dissolved ions and nutrient input (Kempe 1977; Huguet et al. 2011 and references therein). Salinity is around 21 g/kg and pH > 9. Sodium carbonate and sodium chloride equally contribute to the lake salinity with minor contribution of SO_4^{2-}, K^+ and Mg^{2+} (Fig. 5). Calcium results largely depleted. Water column profiles have shown an increase in salinity with depth. The lake floor is characterised by the presence of Tufa towers, huge carbonate microbialites, up to 40 m high, probably the largest on Earth reported so far (Kempe et al. 1991; López-García et al. 2005). The microbialites are externally covered by mats of coccoid cyanobacteria that appear to permineralize in situ with aragonite and inorganically

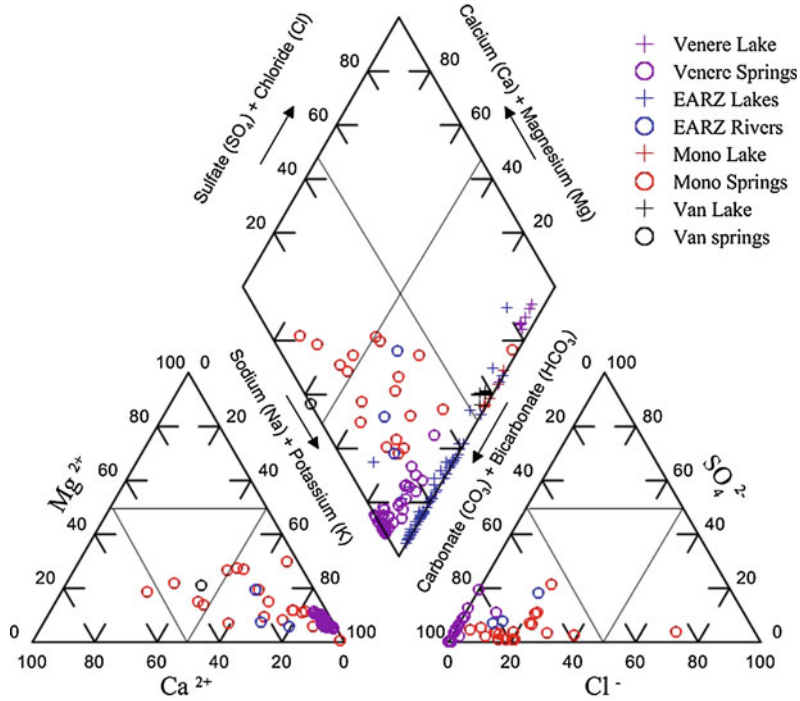

Fig. 5 Piper diagram showing the types and the main components of waters on the basis of concentration in eq/l

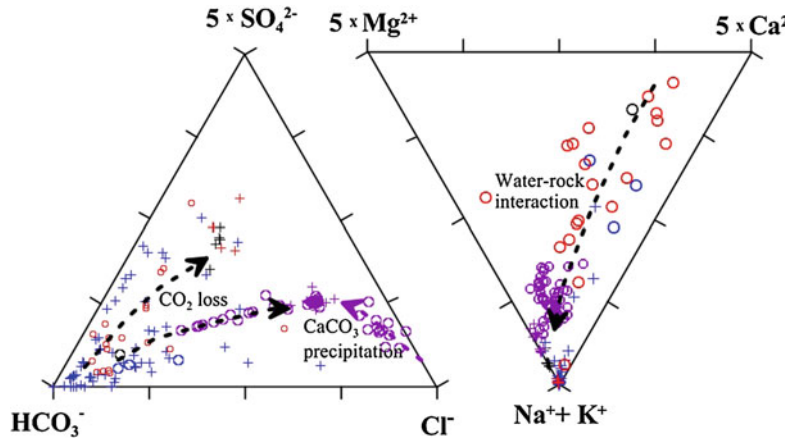

Fig. 6 Major ion *triangular plots* showing the compositional evolution of lake waters from inflow (*crosses*) to lake (*open circles*). *Arrows* indicate the water compositional trend evolution. *Symbols* as in Fig. 2b

precipitated calcite, whereas their interiors are traversed by channels transporting neutral, relatively Ca-enriched spring water flowing into the highly alkaline Ca-poor lake water. The mixing of the two water masses locally induces high calcium carbonate oversaturation and hence carbonate precipitation.

Waters flowing into the lake are predominantly bicarbonate with alkaline elements slightly exceeding alkaline earth elements (Fig. 6; Reimer et al. 2009). Furthermore, the diffuse volcanic CO_2 soil emission in this area contributes to maintain the TDIC/(Ca^{2+} + Mg^{2+}) of the rivers and springs above 1, driving the lake chemistry towards alkaline conditions.

4.2 Lake Natron (Tanzania) and the East African Rift Zone Lakes

The EARZ is the most extensive (4,000 km), NNE-SSW elongated, presently active, continental extensional zone in eastern Africa. The consequence of the extension-related fracturing was the formation of two sub parallel elongate shallow depressions, stretching from Ethiopia to Tanzania, now filled with volcanic rocks, volcano-clastic sediments, and fresh and saline lakes. The rift branch topography is characterised by half-graben basins associated with steeply-dipping border faults (Dawson 2008; Bergner et al. 2009; Corti 2009). The EARZ contains features such as snow-capped Kilimanjaro, the highest mountain on the African continent; Ngorongoro, one of the largest calderas on Earth; and active volcanoes like Nyiragongo, Nyamuragira (Tedesco et al. 2011) and Oldoinyo Lengai (Kervyn et al. 2008), which is unique for its extrusion of alkali carbonatites.

Most parts of the EARZ can be considered a closed basin with no obvious outflow where groundwater and seasonal streams flowing from the surrounding highlands collect to form (semi) permanent standing basin lakes. The EARZ lakes vary in size from large and deep lakes such as Turkana Lake (6,750 km^2 in surface and 109 m deep, Yuretich and Cerling 1983; Cerling 1996), to shallow and relatively large lakes such as Magadi Lake (100 km^2 and ~1 m depth, Jones et al. 1977), to many very small lakes.

While some of the lakes are mainly fed by rivers (Turkana, Baringo, Nakuru, Natron), others receive a considerable part of the inflow from springs often fed by hydrothermal systems (Logipi, Bogoria, Elementeita, Magadi). Sometimes, surface evaporation rates exceed the rate of water inflow allowing the dissolved minerals to concentrate into caustic alkaline brines with a pH up to 12.

Total salts vary from about 5 % in the northern lakes (Bogoria, Nakuru, Elmenteita, Sonachi) up to halite saturation (>30 %) in the southern ones (Magadi and Natron Lakes). EARZ lake waters are prevalently Na–Cl and Na–HCO_3–CO_3 (Fig. 5). The chemistry (Fig. 6) can be explained in terms of both chemical

weathering of rocks and evaporative phenomena. According to Kilham (1971), in the relatively humid areas along the rift, high temperature and rain water support the dissolution of the more soluble minerals of volcanic rocks (e.g. nepheline) and, on the contrary, in dry areas weathering is nearly absent and waters initially have a composition similar to rain water. Consequently, Na–HCO_3–CO_3 lakes develop in relatively humid basins whereas Na–Cl lakes develop in the more arid basins. Most of the alkalinity is acquired by hydrolysis of volcanic rocks (Eqs. 1–3), mainly glass and lavas, generating high concentrations of Na^+, SiO_2 and TDIC, which are reflected in the Na–CO_3 or Na–CO_3–Cl type chemical composition (Figs. 1 and 2) (Jones and Deocampo 2003). Further concentration of the lake waters (>30 %) causes the precipitation of halite, carbonates (trona and gaylussite) or silicates (Na-silicates and zeolites).

Lake Natron (Fig. 4b) is located in a closed drainage system in northern Tanzania, in the eastern branch of the East African Rift. The lake lies at 610 m asl, is 22–35 km wide and 50–75 km long, with a surface area of about 1,100 km^2. The lake is only 3–4 m deep and the evaporation rate is up to 20 mm/d (Dawson 2008). The lake is fed by four rivers: Ewaso Nyiro, Peninj, Moinik and Engare Sero. It is surrounded by escarpments and volcanoes. Pliocene to Recent volcanism resulted in basaltic and trachytic lavas to trachyandesitic and carbonatitic ashes, most recently originating from the active volcano Oldoinyo Lengai. Several mineral-rich hot springs enter on the western and eastern shores of the lake (Dawson 2008). Its waters are rich in sodium carbonate/bicarbonate, NaCl (Figs. 5 and 6) and silica, with a pH near 9.5 (Howell 1972; Dawson 2008 and references therein). The water of Lake Natron is so rich in dissolved sodium carbonate that it often feels viscous to touch.

4.3 Mono Lake (California, USA)

Mono Lake (Fig. 4c), a great endorheic and monomictic (Christenson et al., this issue) alkaline salt lake, is located on the western edge of the Great Basin in northeastern California bounded to the west by Sierra Nevada fault, to the north by the Body Hills, to the east by the Anchorite Hills and Cowtrach Mountains, and to the south by Long Valley Caldera and other rhyolitic, andesitic and basaltic volcanoes (Sahajpal et al. 2011). Mono basin itself contains young volcanic centres: Mono-Inyo craters, where the lake is located, and Paoha and Negit Islands inside the lake. The most recent eruptions in the area occurred at Paoha Island about 200 years ago (Kelleher and Cameron 1990)

Mono Lake is a terminal lake, lies at ca 1,940 m asl, is 25 km wide along its east-west axis, and has a surface area of 150–180 km^2 (depending of the evaporative status) and a maximum depth of 46 m. Snow melt from Sierra Nevada (85 %) and perennial hot and cold springs feed the lake together with a negligible amount of direct rain waters (Sahajpal et al. 2011, and references therein). Evaporation represents the main lake (and groundwater) water loss (Connell and Dreiss 1995).

The lake is fed by both alkaline and acidic (pH $\sim$ 6) springs, with different salinities in function of their origin (Neumann and Dreiss 1995). As in other closed basin lakes, changes in hydrology strongly affect the water chemistry of Mono Lake, highlighted by the salinities ranging from 20 to 100 g/l. Differences are mostly due to the sampling point (e.g. nearness to more diluted springs coming from Sierra Nevada) and evaporation processes during the hot season. Mono Lake waters are strongly alkaline (pH up to 9.8, Whiticar and Suess 1998), of Na-Cl type (Fig. 6) and the ion abundance is $Na > Cl > HCO_3 > SO_4$. Potassium is removed by ion exchange in which K^+ displaces Ca^{2+} in clays or volcanic glasses in ash layers (Connell and Dreiss 1995). Calcium is removed by precipitation of ikaite ($CaCO_3 \cdot 6H_2O$) rather then calcite, whose precipitation is inhibited by high concentration of orthophosphate (Bishoff et al. 1993).

Mixing between high-calcium groundwaters discharging into the lake and high bicarbonate lake waters causes the development of spectacular up to 3 m diameter tufa towers.

4.4 Specchio di Venere Lake (Pantelleria Island, Southern Italy)

Pantelleria Island (Fig. 4d) is a Pleistocene stratovolcano located in the NW–SE trending continental rift between North Africa and Sicily, Italy. Pantelleria represents the emerged part of a 836 m asl high volcanic structure, extending below sea-level to ~1,200 m depth. The structural setting of the island is defined by both tectonic and volcano-tectonic lineaments including regional faults and fractures with the same orientation as the rift (Boccaletti et al. 1987; Acocella et al. 2004; Mattia et al. 2007; Rotolo et al. 2007; Civile et al. 2008; Catalano et al. 2009; Civile et al. 2010). Specchio di Venere Lake (called also Venere lake or Bagno dell'Acqua) is a small alkaline saline lake located in a closed basin on the northern side of Pantelleria Island (Azzaro et al. 1983; Dongarrà et al. 1983; Duchi et al. 1994; Aiuppa et al. 2007; Cangemi et al. 2010; Pecoraino et al. 2011). Its basin is delimited in the northern part by the scarp of the Cinque Denti caldera and to the south by the slopes of domes and cones (Mt Gelfiser) which are the expression of Holocene volcanic activity.

Specchio di Venere Lake is sub-squared in shape, around 450 m long and 350 m wide, and has a maximum depth of ~12 m. The water depth and the shoreline are subject to seasonal adjustments as a function of the annual hydrological balance. In the period 1992–1996 its surface area varied between 0.136 and 0.2 km^2 (Aiuppa et al. 2007). Specchio di Venere Lake can occasionally undergo thermal and chemical stratification but due to its small water volume these are generally short lasting events and atmospheric disturbances such as strong wind are capable to totally remix its waters (Aiuppa et al. 2007). The lake is mainly fed by rainfall and by the inflow of thermal springs. The morphology of the lake floor is quite irregular. In correspondence with springs inflowing at the lake floor, in particular in the shallow south-western sector, Cangemi et al. (2010) recognise some structures related to the formation of siliceous stromatolites.

Lake water presents high Cl^- and alkali contents (Fig. 6), high electrical conductivity (up to 40 mS/cm^2) and pH values up to 9.3. The high concentrations in alkali, mainly Na^+, are the result of notable interactions between thermal waters and Na-rich peralkaline rhyolite (Pantellerite). Due to the small volume of water, change in hydrological and meteorological/rainfall inputs strongly control the composition of lake waters (Pecoraino et al. 2011).

Despite the large amount of bubbling CO_2 and the high content of HCO_3^- in inflowing springs, the TDIC in lake waters is not very high because of the intense precipitation of carbonate minerals. Lake waters are supersaturated with respect to aragonite, calcite, dolomite, accounting for the occurrence of aragonite and dolomite and sporadically calcite in lake sediments and the carbonate layers capping the exposed stromatolites (Azzaro et al. 1983; Cangemi et al. 2010).

5 Microbial Communities in Alkaline Lakes

Abundant microbial life is found in alkaline lakes up to the highest salinities. Because of the unusual characteristics of alkaline, hypersaline environments their bacterial communities have been studied for many years, in part in the quest for commercially valuable biotechnology. These studies have been summarized by Grant et al. (1990) and Oren (2002). A wealth of interesting microorganisms can be found in the soda lakes. Halophilic and alkaliphilic microorganisms are found in all three domains of life: *Archaea*, *Bacteria* and *Eucarya*. They have already made a large impact in the application of biotechnology for the manufacturing of mass-market consumer products. "Biological detergents" contain enzymes that have usually been obtained from alkaliphilic or alkalitolerant bacteria. The current proportion of total world enzyme production destined for the laundry detergents market

comfortably exceeds 25 %, and there are other possible applications in food and waste treatment industries (Grant et al. 1990).

In those cases in which the total dissolved salts concentration exceeds 250–300 g/l such as in Lake Magadi and its solar salterns and in some of the Wadi Natrun lakes, halophilic and alkaliphilic Archaea of the order Halobacteriales often impart a red colour to the brines. The occurrence of red brines is a phenomenon long known in salt production from sea water. The first descriptions may date back to about 2700 BC in the ancient Chinese literature (Oren 2002) and it has been suggested that the first Plague of Egypt (Exodus 7: 17–25), in which the water of the Nile "turned into blood", refers to such red waters. The first scientific descriptions of red bacteria in brines were made at the beginning of the 20th century, although important scientific findings about the microbiology of alkaline and hypersaline lakes were obtained since the second half of the preceding century (Oren 2002).

One of the most impressive characteristics of alkaline lakes is their extremely high primary productivity despite the extreme nature of such environments. Compared to the global mean gross primary productivity for streams and lakes (Whittaker and Likens 1972) of about 0.6 g C m^{-2} day^{-1}, alkaline lakes are characterised by productivity rates exceeding 10 g C m^{-2} day^{-1} (Talling et al. 1973; Melack and Kilham 1974). They are probably the most productive, naturally occurring aquatic environments, presumably because of the relatively high ambient temperatures, high light intensities, availability of phosphate and unlimited access to CO_2 in these carbonate-rich waters (Melack and Kilham 1974; Grant et al. 1990). They are also regarded as naturally eutrophic reservoirs and, like all eutrophic bodies of water, they feature considerable microbial diversity (Zavarzin et al. 1999). The soda lakes of the EARZ are shown to support a dense and diverse population of aerobic, organotrophic, halophilic, alkaliphilic and alkali-tolerant representatives of major bacterial and archaeal phyla (reviewed by Duckworth et al. 1996; Jones et al. 1998; Grant et al. 1999; Zavarzin et al. 1999). The primary productivity is generally due to the presence of dense populations of cyanobacteria (up to 13,000 cyanobacterial filaments per ml, Talling et al. 1973; Melack and Kilham 1974). In extreme cases, the blooms may consist almost entirely of one species, usually *Spirulina* sp. These particular cyanobacteria are the principal food of the immense flocks of flamingos that inhabit the Rift Valley.

In contrast to aerobic habitats, the anaerobic alkaline environments received less attention. But anaerobic processes have a significant role because of dissolved O_2 shortage consequence of the very high productivity of these environments (Jones et al. 1998). Lacustrine muds are black and anoxic, implying the presence of sulfides and of specific anaerobic populations of sulfate-reducing bacteria.

The nutrient cycle in soda lakes is summarised in Fig. 7 (Jones et al. 1998).

Like in other environments characterised by extreme ecological conditions also in hypersaline, closed basin soda lakes and their remnant brines microbial life coping with high concentrations of toxic elements can be found. Extreme contents of arsenic occur for example in Mono Lake (Oremland et al. 2004). Although arsenic is a well-known toxicant to eukaryotes and prokaryotes alike, some prokaryotes have evolved biochemical mechanisms to exploit arsenic oxyanions (i.e., arsenate and arsenite); they can use them either as an electron acceptor for anaerobic respiration (arsenate), or as an electron donor (arsenite) to support chemoautotrophic fixation of CO_2 into cell carbon. Despite the freshwater or marine ecosystems, these processes may assume quantitative significance with respect to the carbon cycle in arsenic-rich soda lakes (Oremland et al. 2004).

Furthermore, it was recently discovered that also Se- and Te-oxyanions are used as respiratory electron acceptors to sustain anaerobic growth of certain bacteria in the sediments of Mono Lake (Baesman et al. 2009). But most intriguing was the discovery in the same environment of "a bacterium that can grow by using arsenic instead of phosphorus" (Wolfe-Simon et al. 2011). Although some doubts have meanwhile arisen about these findings (Foster 2011) it testifies for

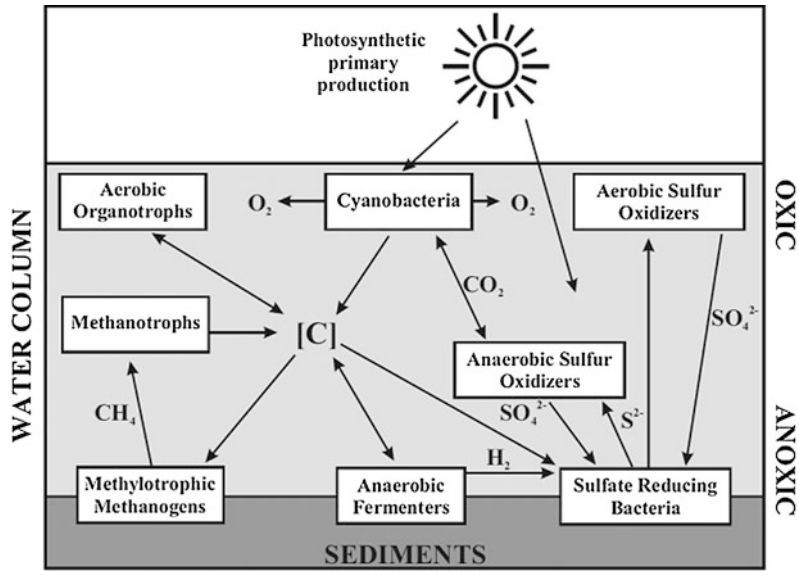

Fig. 7 Flow diagram of the nutrient cycle in soda lakes (modified after Jones et al. 1998)

the highly interesting microbial communities found in such extreme environments.

6 Summary

Alkaline lakes are a peculiar type of saline or hypersaline lakes characterised by pH values higher than 9 and whose chemical composition is characterised by Na^+ as the main cation and by the presence of high HCO_3^- and CO_3^{2-} contents, although sometimes the main anionic species could be Cl^-, or rarely SO_4^{2-}. The evolution of these lakes towards alkaline conditions is favoured by an environment in which hydrologic (endorheic) and climatic (arid or semiarid) factors cause evaporative concentration of its waters. Due to the fact that earth-alkaline carbonates are the first solid phases to reach oversaturation, the initial ratio between the total dissolved inorganic carbon (TDIC) to the main earth-alkaline elements (Ca^{2+} and Mg^{2+}) of the starting dilute waters is very important in driving the subsequent evolution of the lake waters. TDIC/(Ca^{2+}+Mg^{2+}) ratios much higher than 1 will leave the waters enriched in TDIC and devoid of Ca^{2+} and Mg^{2+} which is the typical composition of alkaline lakes. If the necessary hydrologic and climatic conditions are present, quiescent or recently extinct volcanic areas are the most favourable candidates in hosting waters that will evolve towards alkaline conditions. In these areas, where acidic magmatic gases do not have the possibility to reach the lake waters, there is an abundant input of endogenous CO_2 that will contribute to the increase of TDIC and the weathering of the volcanic silicate rocks will release to the waters prevailingly alkaline elements either because earth-alkaline elements are rare (silicic rocks) or are scarcely mobile (mafic rocks).

Alkaline lakes are also characterised by abundant and diversified microbial life. They are among the most productive, naturally occurring aquatic environments. Productivity rates exceeding 10 g C m^{-2} day^{-1} are sustained by euthrophic conditions, relatively high ambient temperatures, high light intensities and unlimited access to CO_2. Microbes living in alkaline lakes have found applications in the production of enzymes for detergents, as animal feed (*Spirulina*) and for waste treatment industries.

Due to evaporative concentration and high solubility in alkaline environments many trace elements can reach very high contents in alkaline hypersaline lakes. This could be of environmental concern in the case of toxic elements but also represent an important mineral resource (Li, B, REE).

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References

Acocella V, Funiciello R, Marotta E, Orsi G, de Vita S (2004) The role of extensional structures on experimental calderas and resurgence. J Volcanol Geotherm Res 129:199–217. doi:10.1016/S0377-0273(03)00240-3

Aguilera E, Chiodini G, Cioni R, Guidi M, Marini L, Raco B (2000) Water chemistry of Lake quilotoa (Ecuador) and assessment of natural hazards. J Volcanol Geotherm Res 97:271–285

Aiuppa A, D'Alessandro W, Gurrieri S, Madonia P, Parello F (2007) Hydrologic and geochemical survey of the lake specchio di venere (Pantelleria Island, Southern Italy). Environ Geol 53:903–913. doi:10.1007/s00254-007-0702-1

Anderson GC (1958) Seasonal characteristics of two saline lakes in Washington. Limnol Oceanogr 3:51–68

Aydar E, Gourgaud A, Ulusoy I, Digonnet F, Labazuy P, Sen E, Bayhan H, Kurttas T, Tolluoglu AU (2003) Morphological analysis of active mount nemrut stratovolcano, eastern Turkey: evidences and possible impact areas of future eruptions. J Volcanol Geotherm Res 123:301–312

Ayenew T (2008) The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian rift and adjacent highlands. Environ Geol 54:1313–1324. doi:10.1007/s00254-007-0914-4

Azzaro E, Badalamenti F, Dongarrà G, Hauser S (1983) Geochemical and mineralogical studies of lake specchio di Venere, Pantelleria Island, Italy. Chem Geol 40:149–165

Baesman SM, Stolz JF, Kulp TR, Oremland RS (2009) Enrichment and isolation of *Bacillus beveridgei* sp. nov, a facultative anaerobic haloalkaliphile from Mono Lake, California, that respires oxyanions of tellurium, selenium, and arsenic. Extremophiles 13:695–705. doi:10.1007/s00792-009-0257-z

Bergner AGN, Strecker MR, Trauth MH, Deino A, Gasse F, Blisniuk P, Duhnforth M (2009) Tectonic and climatic control on evolution of rift lakes in the central Kenya rift, East Africa. Quatern Sci Rev 28:2804–2816. doi:10.1016/j.quascirev.2009.07.008

Bischoff JL, Stine S, Rosenbauer RJ, Fitzpatrick JA (1993) Ikaite precipitation by mixing of shoreline springs and lake water, mono lake, California. Geochim Cosmochim Acta 57:3855–3865

Bischoff JL, Israde-Alcantara I, Garduño-Monroy VH, Shanks WC (2004) The springs of lake patzcuaro: chemistry, salt-balance and implications for the water balance of the lake. Appl Geochem 19:1827–1835. doi:10.1016/j.apgeochem.2004.04.003

Boccaletti M, Cello G, Tortorici L (1987) Transtensional tectonics in the sicily channel. J Struct Geol 9–7:869–876

Bowen BB, Benison KC (2009) Geochemical characteristics of naturally acid and alkaline saline lakes in southern Western Australia. Appl Geoch 24:268–284. doi:10.1016/j.apgeochem.2008.11.013

Cangemi M, Bellanca A, Borin S, Hopkinson L, Mapelli F, Neri R (2010) The genesis of actively growing siliceous stromatolites: evidence from lake specchio di venere, Pantelleria Island, Italy. Chem Geol 276:318–330. doi:10.1016/j.chemgeo.2010.06.017

Catalano S, De Guidi G, Lanzafame G, Monaco C, Tortorici L (2009) Late quaternary deformation on the island on Pantelleria: new constraints for the recent tectonic evolution of the sicily channel rift (Southern Italy). J Geodyn 48:75–82. doi:10.1016/j.jog.2009.06.005

Castenholz RW (1960) seasonal changes in the attached algae of freshwater and saline lakes in the lower grand coulee, Washington. Limnol Oceanogr 5:1–28

Cerling TE (1996) Pore water chemistry of an alkaline lake: Lake Turkana. In: Johnson C, Odada EO (eds) The Limnology, Climatology, and Paleoclimatology of the East African lakes. Gordon and Breach Science Publishers/Overseas Publishers Association, Amsterdam, The Netherlands, pp 225–240

Christenson BW, Tassi F (this issue) Gas in volcanic lake environments

Christenson BW, Németh K, Rouwet D, Tassi F, Vandemeulebrouck J, Varekamp JC (this issue) Volcanic lakes

Christol A, Kuzucuoglu C, Fort M, Karabiyikoglu M, Mouralis D, Brunstein D, Dogu AF, Akkopru E, Fontugne M, Zorer H (2008) Apports de l'etude geomorphologique des terrasses fluvio-lacustresdu lac de Van (Turquie) à la connaissance des paleoenvironnements en Anatolie orientale. In: Galop D (ed) Paysages et Environnements: De la Reconstitutiondu Passé aux Modeles Prospectifs, Annales litteraires, Serie 'Environnement, societes et archeologie'. PU de Franche-Comt Besancon

Civile D, Lodolo E, Tortorici L, Lanzafame G, Brancolini G (2008) Relationships between magmatism and tectonics in a continental rift: the pantelleria Island region (sicily channel, Italy). Mar Geol 251:32–46. doi:10.1016/j.margeo.2008.01.009

Civile D, Lodolo E, Accettella D, Geletti R, Ben-Avraham Z, Deponte M, Facchin L, Ramella R, Romeo R (2010) The pantelleria graben (Sicily channel, central mediterranean): an example of intraplate 'passive' rift. Tectonophysics 490:173–183. doi:10.1016/j.tecto.2010.05.008

Connell LT, Dreiss SJ (1995) Chemical evolution of shallow groundwater along the northeast shore of

mono lake, California. Water Resour Res 31:3171–3182
Corti G (2009) Continental rift evolution: from rift initiation to incipient break-up in the main ethiopian rift, East Africa. Earth Sci Rev 96:1–53. doi:10.1016/j.earscirev.2009.06.005
Dawson JB (2008) The Gregory rift valley and neogene–recent volcanoes of Northern Tanzania. Geological Society, London, Memoirs: 33. doi: 10.1144/M33.1
Degens ET, Kurtman F (1978) The Geology of Lake Van. Publ. N 169, Mineral Research and Exploration Institute (MTA) 169 Ankara, Turkey, 158 p
Degens ET, Wong HK, Kempe S, Kurtman F (1984) A Geological study of lake van, Eastern Turkey. Geol Runds 73–2:701–734
Deocampo DM (2005) Evaporative evolution of surface waters and the role of aqueous CO_2 in magnesium silicate precipitation: lake Eyasi and Ngorongoro Crater, northern Tanzania. S Afr J Geol 108:493–504
Deshmukh KB, Pathak AP, Karuppayil MS (2011) Bacterial diversity of lonar soda lake of India. Indian J Microbiol 51(1):107–111. doi:10.1007/s12088-011-0159-5
Dongarra G, Hauser S, Alaimo R, Carapezza M, Tonani F (1983) Hot waters on pantelleria Island. Geochemical features and preliminary geothermal investigations. Geothermics 12:49–63
Duchi V, Campana ME, Minissale A, Thompson M (1994) Geochemistry of thermal fluids on the volcanic isle of pantelleria, Southern Italy. Appl Geoch 9:147–160
Duckworth AW, Grant WD, Jones BE, van Steenbergen R (1996) Phylogenetic diversity of soda lake alkaliphiles. FEMS Microbiol Ecol 19:181–191
Eugster HP, Hardie LA (1978) Saline lakes. In: Lerman A (ed) Lakes: chemistry, geology, physics. Springer, New York
Eugster HP, Jones BF (1979) Behavior of major solutes during closed-basin brine evolution. Am J Sci 279:609–631
Foster PL (2011) Comment on a bacterium that can grow by using arsenic instead of phosphorus. Science 332:1149. doi:10.1126/science1201551
Garrels RM, Mackenzie FT (1967) Origin of the chemical composition of some springs and lakes equilibrium concepts in natural water systems. Adv Chem 67:222–242
Giggenbach WF (1990) Water and gas chemistry of lake nyos and its bearing on the eruptive process. J Volcanol Geotherm Res 42:337–362
Gizaw B (1996) The origin of high bicarbonate and fluoride concentrations in waters of the main ethiopian rift valley, East African rift system. J Afr Earth Sci 22:391–402
Grant WD, Tindall BJ (1986) The alkaline saline environment. In: Herbert RA, Codd GA (eds) Microbes in extreme environments. Academic Press, London, pp 25–54
Grant S, Grant WD, Jones BE, Kato C, Li L (1999) Novel archaeal phylotypes from an East African alkaline saltern. Extremophiles 3:139–145
Grant WD, Mwatha WE, Jones BE (1990) Alkaliphiles: ecology, diversity, and applications. FEMS Microbiol Rev 75:255–270. doi:10.1111/j1574-69681990tb04099x
Green WJ, Lyons WB (2009) The Saline lakes of the mcmurdo dry valleys, Antarctica. Aquat Geochem 15:321–348. doi:10.1007/s10498-008-9052-1
Hardie LA, Eugster HP (1970) The evolution of closed-basin brines. Mineral Soc Am, Special Paper 3:273–290
Howell FC (1972) Pliocene/Pleistocene hominidae in eastern Africa: absolute and relative ages. In: Bishop WW and Miller JA (eds) Calibration of hominoid evolution. Scottish Academic Press, Edinburgh, pp 331–368
Huguet C, Fietz S, Stockhecke M, Sturm M, Anselmetti FS, Rosell-Mele A (2011) Biomarker seasonality study in lake van, Turkey. Org Geochem 42:1289–1298
Johannesson KH, Lyons WB, Bird DA (1994) Rare earth element concentrations and speciation in alkaline lakes from the western USA. Geophys Res Lett 21(9):773–776. doi:10.1029/94GL00005
Jones BE, Grant WD, Duckworth AW, Owenson GG (1998) Microbial diversity of soda lakes. Extremophiles 2:191–200
Jones BF (1966) Geochemical evolution of closed basin water in the western Great Basin. In: Rau JL (ed) Proceedings of the second symposium on salt. Geology, Geochemistry, Mining Northern Ohio Geological Society, Cleveland, pp 181–200
Jones BF, Eugster HP, Rettig SL (1977) Hydrochemistry of the lake magadi basin, Kenya. Geochim Cosmichim Acta 41:53–72
Jones BF, Deocampo DM (2003) Geochemistry of saline lakes. In: Drever JI, Holland HD, Turekian KK (eds) Freshwater geochemistry, weathering and soils. Treatise on geochemistry, vol 5, pp 393–424
Jones BF, Naftz DL, Spencer RJ, Oviatt CG (2009) Geochemical evolution of great Salt Lake, Utah, USA. Aquat Geochem 15:95–121. doi:10.1007/s10498-008-9047-y
Kelleher PC, Cameron KL (1990) The geochemistry of the mono craters-mono lake Islands volcanic complex, eastern California. J Geophys Res 95(B11):17643–17659
Kempe S (1977) Hydrographie, Warven-Chronologie und organische geochemie des Van Sees, Ost-Turkei. Geologisch-Palaontologischen Institut der Universität Hamburg, MGPIUA 47:125–228
Kempe S, Kazmierczak J, Landmann G, Konuk T, Reimer A, Lipp A (1991) Largest known microbialites discovered in Lake Van, Turkey. Nature 349:605–608
Kervyn M, Ernst GGJ, Klaudius J, Keller J, Kervyn F, Mattsson HB, Belton F, Mbede E, Jacobs P (2008)

Voluminous lava flows at Oldoinyo Lengai in 2006: chronology of events and insights into the shallow magmatic system. Bull Volcanol 70:1069–1086. doi:10.1007/s00445-007-0190-x

Kilham P (1971) The geochemical evolution of closed basin lakes. Geol Soc Am Abstr 3–7:770–772

Kompantseva EI, Bryantseva IA, Komova AV, Namsaraev BB (2007) The structure of phototrophic communities of soda lakes of the southeastern transbaikal region. Mikrobiologiya 76:243–252 (Microbiology (Engl. Transl.) 76:211–219). doi:10.1134/S0026261707020130

Kompantseva EI, Komova AV, Krauzova VI, Kolganova TV, Panteleeva AN (2009) Purple nonsulfur bacteria in weakly and moderately mineralized soda lakes of the southern transbaikal region and northeastern Mongolia. Mikrobiologiya 78:288–296 (Microbiology (Engl. Transl.) 78:246–253).doi: 10.1134/S0026261709020179

Kusakabe M (this issue) Evolution of CO_2 content in Lakes Nyos and Monoun, and sub-lacustrine CO_2-recharge system at Lake Nyos as envisaged from $CO_2/^3He$ ratios and noble gas signatures

Landmann G, Reimer A, Lemcke G, Kempe S (1996) Dating late glacial abrupt climate changes in the 14,570 year long continuous varve record of Lake van, Turkey. Palaeogeogr Palaeocl 122(1–4):107–118

Landmann G, Steinhauser G, Sterba JH, Kempe S, Bichler M (2011) Geochemical fingerprints by activation analysis of tephra layers in lake van sediments, Turkey. Appl Radiat Isot 69:929–935

Long DT, Fegan NE, McKee JD, Lyons WB, Hines ME, Macumber PG (1992) Formation of alunite, jarosite and hydrous iron oxides in a hypersaline system: lake Tyrrell, Victoria, Australia. Chem Geol 96:183–202

Lopez-Garcıa P, Kazmierczak J, Benzerara K, Kempe S, Guyot F, Moreira D (2005) Bacterial diversity and carbonate precipitation in the giant microbialites from the highly alkaline lake van, Turkey. Extremophiles 9:263–274. doi:10.1007/s00792-005-0457-0

Ma L, Lowenstein TK, Russell JM (2011) A brine evolution model and mineralogy of chemical sediments in a volcanic crater, Lake Kitagata, Uganda. Aquat Geochem 17:129–140. doi:10.1007/s10498-010-9108-x

Macintyre S, Melack JM (1982) Meromixis in an equatorial African soda lake. Limnol Oceanogr 27:595–609

Marini L, Vetuschi Zuccolini M, Saldi G (2003) The bimodal pH distribution of volcanic lake waters. J Volcanol Geotherm Res 121:83–98

Mattia M, Bonaccorso A, Guglielmino F (2007) Ground deformations in the Island of pantelleria (Italy): insights into the dynamic of the current intereruptive period. J Geoph Res 112:B11406. doi:10.1029/2006JB004781

Melack JM (1979) Photosynthesis and growth of *Spirulina platensis* (Cyanophyta) in an equatorial lake (Lake Simbi, Kenya). Limnol Oceanogr 24:753–760

Melack JM, Kilham P (1974) Photosynthetic rates of phytoplankton in East African alkaline, saline lakes. Limnol Oceanogr 19:743–755

Neumann K, Dreiss S (1995) Strontium 87/strontium 86 ratios as tracers in groundwater and surface waters in Mono Basin, California. Water Resour Res 31:3183–3193

Ochieng EZ, Lalah JO, Wandiga SO (2007) Analysis of heavy metals in water and surface sediment in five rift valley lakes in Kenya for assessment of recent increase in anthropogenic activities. Bull Environ Contam Toxicol 79:570–576. doi:10.1007/s00128-007-9286-4

Oduor SO, Schagerl M (2007) Temporal trends of ion contents and nutrients in three Kenyan rift valley saline–alkaline lakes and their influence on phytoplankton biomass. Hydrobiologia 584:59–68. doi:10.1007/s10750-007-0605-x

Oremland RS, Stolz JF, Hollibaugh JT (2004) The microbial arsenic cycle in mono lake, California. FEMS Microbiol Ecol 48:15–27

Oren A (2002) Halophilic Microorganisms and their environments cellular origin. Life in extreme habitats and astrobiology, vol 5. Springer, New York. doi: 10.1007/0-306-48053-0

Pecoraino G, Brusca L, D'Alessandro W, Longo M (2011) Geochemical surveys on specchio di venere lake, pantelleria Island, South Italy. In: 5th International limnogeological congress abs, 31 Aug–3 Sept, Konstanz, Germany, p 44

Renaut RW, Tiercelin JJ, Owen RB (1986) Mineral precipitation and diagenesis in the sediments of the lake bogoria basin, Kenya rift valley. Geol Soc London Spec Publ 25:159–175. doi:10.1144/GSLSP19860250114

Reimer A, Landmann G, Kempe S (2009) lake van, eastern Anatolia, hydrochemistry and history. Aquat Geochem 15:195–222. doi:10.1007/s10498-008-9049-9

Risacher F, Fritz B (1991) Geochemistry of Bolivian salars, Lipez, southern Altiplano. Origin of solutes and brine evolution. Geochim Cosmochim Acta 55:687–705

Risacher F, Alonso H, Salazar C (2003) The origin of brines and salts in chilean salars: a hydrochemical review. Earth-Sci Rev 63:249–293. doi:10.1016/S0012-8252(03)00037-0

Rotolo SG, La Felice S, Mangalaviti A, Landi P (2007) Geology and petrochemistry of the recent (<25 ka) silicic volcanism at pantelleria Island. Boll Soc Geol It (Ital J Geosci) 126–2:191–208

Rowe GL Jr, Ohsawa S, Takano B, Brantley SL, Fernández JF, Barquero J (1992) Using crater lake chemistry to predict volcanic activity at poas volcano, costa rica. Bull Volcanol 54:494–503

Sahajpal R, Zimmerman SRH, Datta S, Hemming NG, Hemming SR (2011) Assessing Li and other leachable geochemical proxies for paleo-salinity in lake sediments from the mono basin, CA (USA). Geochim Cosmochim Acta 75:7855–7863

Spencer RJ, Lowenstein TK, Casas E, Pengxi Z (1990) Origin of potash salts and brines in the Qaidam Basin, China. In: Spencer RJ, Chou IM (eds) Fluid-mineral interactions: a tribute to H. P. Eugster. Geochemical Society, San Antonio, pp 395–408

Stumm W (2004) Chemical Processes regulating the composition of lake waters. In: O'Sullivan PE, Reynolds CS (eds) The lakes handbook vol.1, pp 79–106

Talling JF, Wood RB, Prosser MV, Baxter RM (1973) The upper limit of photosynthetic productivity by phytoplankton: evident from Ethiopian soda lakes. Freshwat Biol 3:53–76

Taran Y, Rouwet D, Inguaggiato S, Aiuppa A (2008) Major and trace element geochemistry of neutral and acidic thermal springs at El Chichón volcano, Mexico. Implications for monitoring of the volcanic activity. J Volcanol Geotherm Res 178:224–236

Tedesco D, Vaselli O, Papale P, Carn SA, Voltaggio M, Sawyer GM, Durieux J, Kasereka M, Tassi F (2011) January 2002 volcano-tectonic eruption of Nyiragongo volcano, democratic republic of Congo. J Geophys Res 112:B09202. doi:10.1029/2006JB004762

Tomonaga Y, Brennwald MS, Kipfer R (2011) Spatial distribution and flux of terrigenic He dissolved in the sediment pore water of lake van (Turkey). Geochim Cosmochim Acta 75:2848–2864. doi:10.1016/j.gca.2011.02.038

Utkutu M (2006) Implications for the water level change triggered moderate (M ≥ 4.0) earthquakes in lake van Basin, Eastern Turkey. J Seismol 10:105–117. doi:10.1007/s10950-005-9002-y

Varekamp JC (this issue) The chemical composition and evolution of volcanic lakes

Vaselli O, Tedesco D, Cuoco E, Tassi F (this issue) Are limnic eruptions on the CO_2–CH_4-rich gas reservoir of Lake Kivu (Democratic Republic of the Congo and Rwanda) possible? Insights from physic-chemical and isotopic data

Varekamp JC, Pasternack GB, Rowe GL Jr (2000) Volcanic lake systematics: II chemical constraints. J Volcanol Geotherm Res 97:161–179

Vilaclara G, Chávez M, Lugo A, González H, Gaytán M (1993) Comparative description of crater-lakes basic chemistry in Puebla state, Mexico. Verh Internat Verein Limnol 25:435–440

Volkova NI (1998) Geochemistry of rare elements in waters and sediments of alkaline lakes in the Sasykkul depression, East Pamirs. Chem Geol 147:265–277

Wani AA, Surakasi VP, Siddharth J, Raghavan RG, Patole MS, Ranade D, Shouche YS (2006) Molecular analyses of microbial diversity associated with the lonar soda lake in India: an impact crater in a basalt area. Res Microbiol 157:928–937. doi:10.1016/j.resmic.2006.08.005

Whittaker RH, Likens GE (1972) Carbon in the biota. In: Woodwell GM, Pecan EV (eds) Carbon in the biosphere. AEC symposium series 30

Witham CS (2005) Volcanic disasters and incidents: a new database. J Volcanol Geotherm Res 148:191–233

Whiticar MJ, Suess E (1998) The cold carbonate connection between mono lake, California and the Bransfield Strait, Antarctica. Aquat Geochem 4:429–454

Wolfe-Simon F, Switzer Blum J, Kulp TR, Gordon GW, Hoeft SE, Pett-Ridge J, Stolz JF, Webb SM, Weber PK, Davies PCW, Anbar AD, Oremland RS (2011) A bacterium that can grow by using arsenic instead of phosphorus. Science 332:1163–1166. doi:10.1126/science1197258

Wong HK, Degens ET (1978) The bathymetry of Lake van, Eastern Turkey. In: Degens ET, Kurtman F (eds) Geology of lake van, Miner Res Explor Inst Ankara, Turkey

Yilmaz Y, Guner Y, Saroglu F (1998) Geology of the quaternary volcanic centres of the east Anatolia. J Volcanol Geotherm Res 85:173–210

Yuretich RF, Cerling TE (1983) Hydrogeochemistry of Lake Turkana, Kenya: mass balance and mineral reactions in an alkaline lake. Geochim Cosmochim Acta 47:1099–1109

Zavarzin GA, Zhilina TN, Kevbrin VV (1999) The alkaliphilic microbial community and its functional diversity. Microbiology, translated from Mikrobiologiya 68:503–521

Zhang Q, Kang S, Wang F, Li C, Xu Y (2008) Major ion geochemistry of nam co lake and its sources, Tibetan Plateau. Aquat Geochem 14:321–336. doi:10.1007/s10498-008-9039-y

Zheng M, Liu X (2009) Hydrochemistry of salt lakes of the Qinghai-Tibet Plateau, China. Aquat Geochem 15:293–320. doi:10.1007/s10498-008-9055-y

Zheng M, Tang J, Liu J, Zhang F (1993) Chinese saline lakes. Hydrobiologia 267:23–36